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(54) Title: THIN FILMS HAVING A ROCK-SALT-LIKE STRUCTURE DEPOSITED ON AMORPHOUS SURFACES			
(57) Abstract			
A thin film of material having a rock-salt-like structure is deposited on a smooth amorphous substrate surface by ion beam assisted deposition.			

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THIN FILMS HAVING A ROCK-SALT-LIKE STRUCTURE DEPOSITED ON AMORPHOUS SURFACES

This application claims priority to Provisional Application Serial No. 60/065,324 filed November 13, 1997, entitled "Apparatus and Method for Ion Beam Induced Texturing on Thin Films on Amorphous Substrates".

Brief Description of the Invention

This invention relates generally to thin films. More particularly, this invention relates to thin oxide films of the type having a rock-salt-like structure, deposited on amorphous surfaces with substantially in-plane alignment as well as substantially out-of-plane alignment.

Background of the Invention

There are an increasing number of thin film and thick film materials which, in their application to devices of all types, depend on properties dependent on their anisotropic physical properties, or which require low-angle grain boundaries between grains. Thus, these materials must be deposited in special orientations in order to utilize their properties. The present method of achieving this is to epitaxially deposit onto carefully selected single crystal substrates with matching lattice constants and chemical compatibility.

Ion beam assisted deposition (IBAD) has shown promise as means to produce textured films on non-epitaxial substrates that can then subsequently be used as a structural template for the deposition of other films, eliminating the requirement of single crystalline substrates. The material commonly used has been (100)-oriented

Yttria-Stabilized-Zirconia (YSZ). However, the texturing of (100) YSZ evolves slowly, so a thick film ($>0.5 \mu\text{m}$) is required to achieve good in-plane alignment ($\sim 13^\circ$), limiting the application of YSZ due to high processing time and cost. Other materials, characterized by rock salt and rock salt-like structures, have been considered potentially advantageous for use as templates for forming well textured layers such as superconducting films due to their simple crystal lattice which tends to naturally align with a preferred surface for subsequent growth of textured films ((001) type sheet axis). Rock salt structures tend to have a reasonable lattice match with films such as YBCO and PZT which make them attractive for a variety of electronic and electrical applications. In addition, the simple chemistry of these structures makes them easier to process than the more complex multi-cation structures. By "rock-salt material" is meant a structure having a cF8 Pearson symbol and a B1 Strukturbericht designation. Typical rock salt materials are described, for example, by "Metals Handbook, Ninth Edition", volume 9, p707-711, , which pages are herein incorporated in their entirety by reference, and by C.S. Barrett and T.B. Massalski, "Structure of Metals", McGrawHill, 3rd edition, 1966, p.240-241, , which pages are herein incorporated in their entirety by reference. Exemplary rock salt materials include CaO, SrO, TiN, ZrO, and BaO. By "rock-salt-like material" is meant a material with a crystalline structure with atomic arrangements identical to or similar to that in rock-salt, such as cubic structures with (100) close-packed planes or cubic structures in which a part of the lattice (some planes) has the same atomic arrangement as in rock-salt. Examples, in addition to rock salt materials, are rock-salt superstructure B1, cubic superlattice LI_2 , spinel superlattice H1_1 , and perovskites & perovskite superstructures E2_1 . Exemplary compounds with rock-salt superstructure B1 are LiNiO_2 , and LiInO_2 . Typical cubic superlattice LI_2 compounds are Ni_3Al , Au_3Cu , AlZr_3 , etc. Typical spinel superlattice H1_1 compounds are MgAl_2O_4 , and $\gamma\text{-Al}_2\text{O}_3$. Typical perovskites & perovskite superstructures E2_1 compounds are SrTiO_3 , CaTiO_3 , NdGaO_3 , LaAlO_3 , SrZrO_3 , BaZrO_3 , and SrRuO_3 . However, at present, these materials are typically used either in expensive single crystal forms or as epitaxially grown films which must be produced upon substrates which themselves exhibit a biaxially textured surface.

Objects and Summary of the Invention

It is a general object of the present invention to provide an improved technique for producing textured films of materials having a rock-salt structure on amorphous substrates.

It is another object of the present invention to provide a technique for producing textured films having a rock salt-like structure on amorphous substrates.

It is a further object of the present invention to provide an economical method of producing textured films on an amorphous substrate.

It is a further object of the present invention to provide an economical thin film buffer layer for the deposition of high temperature superconductor material.

The present invention provides a method of forming textured thin films having a rock-salt-like structure on an amorphous surface employing ion beam assisted deposition of the thin film material and a method of forming composite articles including multiple film layers having substantial alignment both in-plane and out-of-plane.

In one aspect, the invention is a method of forming a composite article by forming a buffer layer including a first thin film formed on a smooth amorphous surface of a substrate from a material having a rock-salt-like structure and substantial alignment both in-plane and out-of-plane, and forming a second film having substantial alignment both in-plane and out-of-plane on a surface of said buffer layer, wherein said first film provides a template for the epitaxial growth of said second film. The first thin film is formed by ion-beam assisted deposition of the rock-salt-like material under first conditions of temperature, rock-salt-like material evaporation rate, ion energy and flux selected to promote formation of in-plane aligned crystallites of the rock-salt-like material on the smooth amorphous surface at the nucleation stage of film formation and subsequent pseudo-columnar growth of columns of the crystallites, resulting in substantial alignment both in-plane and out-of-plane.

Typically, the ion beam assistance is ended after the thickness of said first film is such that said smooth amorphous surface is substantially covered with said in-plane aligned crystallites and before the thickness of said first film is about twice the thickness at which said surface is substantially covered with said in-plane aligned crystallites. In one aspect, a homo-epitaxial layer of the rock salt-like material is then formed on the

surface of the first film by deposition of the same rock salt-like material under second conditions of temperature and rock salt-like material evaporation rate which are elevated in relation to the first conditions to increase the thickness of the buffer layer. The first film provides a template for the epitaxial growth of the homoepitaxial layer. In other aspects, the method may include formation of additional buffer layer films of additional materials deposited after formation of the first film, and the first film will provide a template for the epitaxial growth of the these films.

In another aspect, the invention features an article, including a substrate with at least one smooth amorphous surface, a buffer layer comprising a first thin film formed on said smooth amorphous surface of said substrate from a material having a rock-salt-like structure, and a second film formed on a surface of said buffer layer. The first film has substantial alignment both in-plane and out-of-plane; and provides a template for the epitaxial growth of the second film. The second film may be formed from a material selected from the group consisting of superconductors, semiconductors, photovoltaic materials, magnetic materials, and precursors of superconductors. Typically, the RMS of the smooth amorphous surface is less than about 100 angstroms.

In some aspects, the entire substrate is amorphous, as for example, Metglas or α - Si_3N_4 . In other aspects, the substrate is a polycrystalline non-amorphous base structure with a smooth amorphous surface layer. In some aspects, this layer may be chemically identical to the base structure. For example, polycrystalline Ni in some forms is an intrinsically an ordered structure with an amorphous surface. The desired amorphous surface may also be created, for example, by laser glazing, ion damage, or high rate mechanical deformation. In other aspects, the layer is not chemically identical to the base structure and may be created, for example, by deposition or ion implantation. Suitable base structures include nickel alloys, and preferably alloys comprising nickel as a primary component, including Hastelloy and Metglas. In some aspects, the rock-salt-like material is a rock-salt material.

In a preferred embodiment, the rock-salt material is MgO and the thickness of the first film is less than about 200 Angstroms, preferably less than about 150 Angstroms, but greater than about 20 Angstroms. Its alignment is better than about 13 degrees. The buffer layer may include additional films, deposited homoepitaxially or

heteroepitaxially, and the first film will provide a template for the epitaxial growth of all subsequently deposited films.

The second film may be formed from a material selected from the group consisting of superconductors, semiconductors, photovoltaic materials, magnetic materials, and precursors of superconductors.

Brief Description of the Drawings

For a better understanding of the nature of the invention, attention is directed toward the following detailed description taken in conjunction with the accompanying drawings, in which:

Figure 1 schematically shows an apparatus for carrying out the present invention.

Figure 2 shows a textured MgO film formed on an amorphous silicon nitride substrate layer.

Figure 3 is an enlarged view of a buffer layer or film deposited in accordance with the prior art.

Figure 4 is an enlarged view of a buffer layer or film deposited in accordance with the present invention.

Figures 5(a) - 5(f) show real time reflection high energy electron diffraction (RHEED) observation of an ion beam assisted deposition (IBAD) (deposited at room temperature) and homo-epi MgO film (deposited at 600°C), in which (a) to (c) are IBAD MgO at 20, 50 and 100 Å respectively, and (d) to (f) are homo-epi MgO at 100, 400 and 800 Å respectively.

Figures 6(a) and 6(b) are X-ray diffraction scans of the MgO film shown in Figure 5 (100Å IBAD and 800Å homo-epi film): (a) ω -scan of the MgO (200) peak and (b) ϕ -scan of the MgO (220) peak.

Figure 7 is a X-TEM of an IBAD MgO (deposited at 300°C), in which the ion beam was incident at roughly 45° with respect to the normals of the substrate and image planes.

Figure 8 is an X-TEM of a high temperature superconductor film deposited upon a buffer layer or film formed in accordance with the present invention.

Detailed Description of the Preferred Embodiment of the Invention

The invention will be described in connection with the formation of in-plane textured (100) MgO films on a smooth amorphous Si_3N_4 surface by ion beam assisted deposition (IBAD). However, it will be apparent that films of other materials having a rock salt-like structure can be deposited on other smooth amorphous surfaces.

Referring to Figures 1 and 2, a substrate 11 having an amorphous Si_3N_4 surface layer 12 formed on a single crystal silicon member 13 is positioned to receive MgO vapor from the source 14, to deposit a textured MgO film 16. The MgO is evaporated from the source by an electron beam. The deposition rate can be, for example, between 1.0\AA and 4.4\AA per second. The substrate temperature can be between room temperature or less and 400°C . Other MgO deposition methods such as sputtering or pulsed laser deposition may be used to deposit the MgO film onto the amorphous surface layer 12. Other amorphous surface layers such as SiO_2 can be used. Figure 3 shows a MgO film deposited without ion beam assistance. The rock salt-like structure deposits with an out-of-plane alignment of the (001) plane. The in-plane orientation of the crystals is random as shown by the lines 17, Figure 3.

In accordance with the present invention, an ion beam 18 is projected onto the surface of the substrate at an angle α with respect to the substrate normal by an ion source 19. For example, the ion source can be a Kaufman 3 cm ion source. The ion energy can be between 200 and 1200 eV. The angle α can be between 10° and 80° .

The diffraction pattern of the film is monitored in real time using a reflection high energy electron diffraction apparatus (RHEED) (not shown) which projects a RHEED beam 21 onto the deposition surface. A Faraday cup and quartz crystal monitor (not shown) are used to monitor the ion flux and evaporation rate of the material being deposited.

In one example MgO IBAD films 16 were deposited on an amorphous Si_3N_4 layer 12 carried by a silicon wafer 13, Figure 2. The diffraction pattern of the film surface was monitored as it was deposited using RHEED. The ion source was an argon ion source Ar^+ at 700eV ion energy. The flux ranged from $110\text{--}120\ \mu\text{A}/\text{cm}^2$. The angle α between the ion beam and the substrate normal was 45° , which is an open or channel direction for (100) MgO. The evaporation rate of MgO was selected by monitoring the appearance of the MgO diffraction patterns in RHEED. In-plane

textured MgO films were obtained from room temperature (RT) to 300°C. For an RT deposition, the best alignment was obtained with a 1.5Å/sec evaporation rate. Figure 4 illustrates the alignment of the crystals.

Figures 5(a) - (f) show a typical texturing or deposition sequence observed with the *in situ* RHEED. When the proper deposition conditions are set, the RHEED pattern changes from a diffused-scattering pattern (from the amorphous Si₃N₄ substrate) to a crystalline pattern of MgO at about 20Å film thickness, Figure 1(a), which is the limiting diffraction thickness of the RHEED. The pattern suggests that the MgO molecules form well-aligned small 3D crystallites right at the inception of the deposition, i.e. right at the nucleation stage, with (100) planes aligning out-of-plane and the [110] direction facing the ion source. The pattern gradually improved, Figure 1(b), and was optimized at about 100Å, Figure 1(c). At the optimal texture, the ion beam was turned off, the substrate temperature was raised to 600°C and subsequently an 800Å homo-epi MgO was deposited so that the film was thick enough for X-ray diffraction. Based on the RHEED, no obvious additional features were introduced during the homo-epi process, Figures 1(d) to 1(f). X-ray diffraction of the sample, Figure 6(a), indicates a 3° out-of-plane alignment (FWHM of the ω -scan) and Figure 6(b) indicates a 7° in-plane alignment (FWHM of the ϕ -scan).

A cross-sectional TEM (X-TEM) image, Figure 7, reveals the texture development of the IBAD MgO, suggesting that the MgO growth is pseudo-columnar with each column consisting of small 3D crystallites, and that the alignment of these crystallites starts at the MgO/SiN interface. Combining the observations from both TEM and RHEED, a consistent picture emerges in which the MgO texture develops at the beginning of the growth, i.e. the nucleation stage. The optimal thickness of the growth likely corresponds to the point at which the surface of the substrate is fully covered by textured MgO crystallites. After that, the texture improves only slightly and eventually starts to degrade. It has also been observed that both the alignment and coverage of the textured area improved at lower substrate temperature, suggesting that the texturing process is facilitated by the denser and smaller nuclei obtained at lower temperature. This is consistent with the nucleation-texturing mechanism suggested for MgO.

The MgO texturing mechanism and alignment results are very different from those of IBAD (100) YSZ as described earlier. One of the major differences between the two materials is the preferred out-of-plane alignment. At high temperature, the YSZ tends to grow as (111) fiber texture (i.e. the (111) planes aligned out-of-plane while randomly oriented in-plane), and this out-of-plane alignment cannot be changed by the ion beam. Thus, the best chance to obtain (100) YSZ growth is at low temperature. At low temperature, however, the YSZ molecules lack mobility, resulting in a kinetic-limited growth. Without IBAD, either a poorly crystallized film would result or several out-of-plane alignments would co-exist. With IBAD, the ratio of the different out-of-plane orientations depends on the ion energy, deposition methods, etc. and favors (111) when sufficient molecular mobility is obtained, resulting in a complicated texturing process. Conversely, the (100) direction is the preferred out-of-plane alignment for MgO (a rock-salt structure). Thus, the ion beam only needs to align the in-plane orientation, simplifying the texturing process and allowing the texture to appear at early stage. The texture of the IBAD MgO film is totally determined at the initial stage, where the initial texture, substrate condition, and film/substrate interaction become important factors.

The preferred conditions for forming an IBAD MgO layer are: Temperature RT to 400°C; layer thickness about 80Å to about 150Å; ion beam angle $\approx 45^\circ$; amorphous substrate surface; and amorphous surface roughness (RMS) less than about 100Å.

The α -Si₃N₄ substrate layer can be deposited onto a metal alloy such as Hastelloy. The MgO layer is then deposited onto the amorphous substrate as described above. The MgO/ α -Si₃N₄/Hastelloy substrate can then serve as the substrate for the deposit of YBCO to form a high temperature superconductor with a wire or ribbon. Figure 8 is an X-TEM of a YBCO film or layer deposited on an MgO buffer layer formed on Si₃N₄. Table I shows five examples of YBCO/Y₂O₃/YSZ formed on:

- | | |
|-----------|---|
| Sample 1. | YBCO/Y ₂ O ₃ /YSZ/NiO/MgO/MgO(IBAD)/Si ₃ N ₄ /Hastelloy tape
(less polished) |
| Sample 2. | YBCO/Y ₂ O ₃ /YSZ/NiO/MgO/MgO(IBAD)/Si ₃ N ₄ /Poly-YSZ |

- Sample 3. YBCO/Y₂O₃/YSZ/MgO/MgO(IBAD)/Si₃N₄/Hastelloy tape (less polished)
- Sample 4. YBCO/Y₂O₃/YSZ/NiO/MgO/MgO(IBAD)/Si₃N₄/Hastelloy (well-polished)
- Sample 5. YBCO/Y₂O₃/YSZ/NiO/MgO/MgO(IBAD)/Si₃N₄/Hastelloy (well-polished)

TABLE I

Sample No.	SiN roughness (RMS)/film thickness (Å)	MgO in-plane alignment	YSZ in-plane alignment	YBCO in-plane alignment	T _c of YBCO (K)	J _c of YBCO (MA/cm ²)
1	- 20Å/2000Å	***	***	14.3°	-89	0.15
2	-3Å/1000Å	***	***	8°	-89	0.05
3	- 20Å/4000Å	~12°-14°	~12°-14°	~12°-14°	***	0.025
4	- 50Å/1000Å	12.8°	12.8°	12.5°	88	0.33
5	- 20Å/2000Å	12.3°	11.4°	8.2°	87.8	0.30

We have formed highly aligned (based on RHEED) IBAD MgO films on Metglas (Allied Signal) by the same process as described for α -Si₃N₄ substrates. Highly aligned MgO films have also been formed on smooth amorphous surfaces of amorphous α -Si₃N₄, SiO₂, and polycrystalline Ni substrates.

The MgO or the like structural oxides can be deposited on suitably smooth amorphous surfaces of metals, glass fibers, wires, etc. to permit the formation of superconductor layers.

In summary, in-plane textured MgO films on amorphous SiN and other substrates have been described. The films are promising for use as a structural template for the deposition of many materials without the need of single crystalline substrates. This texturing process for MgO is a nucleation process and the alignment is a function of nuclei size and density.

The foregoing description, for purposes of explanation, used specific nomenclature to provide a thorough understanding of the invention. However, it will

be apparent to one skilled in the art that the specific details are not required in order to practice the invention. The foregoing descriptions of specific embodiments of the present invention are presented for purposes of illustration and description. They are not intended to be exhaustive or to limit the invention to the precise forms disclosed, obviously many modifications and variations are possible in view of the above teachings. The embodiments were chosen and described in order to best explain the principles of the invention and its practical applications, to thereby enable others skilled in the art to best utilize the invention and various embodiments with various modifications as are suited to the particular use contemplated. It is intended that the scope of the invention be defined by the following claims and their equivalents.

What is claimed is:

1. An article, comprising:
a substrate having at least one smooth amorphous surface;
a buffer layer comprising a first thin film formed on said amorphous surface of said substrate from a material having a rock-salt-like structure and substantial alignment both in-plane and out-of-plane; and
a second film having substantial alignment both in-plane and out-of-plane formed on a surface of said buffer layer, wherein said first film provides a template for the epitaxial growth of said second film.
2. An article according to claim 1 wherein said second film is formed from a material selected from the group consisting of superconductors, semiconductors, photovoltaic materials, magnetic materials, and precursors of superconductors.
3. An article according to claim 1 wherein the RMS of said smooth surface is less than about 100 angstroms.
4. An article according to claim 1 wherein the substrate comprises a polycrystalline non-amorphous base structure having an amorphous surface layer.
5. The article according to claim 4, wherein the base structure is formed from a material selected from the group consisting of alloys comprising nickel.
6. The article according to claim 5, wherein the base structure is formed from a material selected from the group consisting of alloys comprising nickel as a primary component.
7. The article according to claim 6, wherein the base structure is formed from Hastelloy.
8. The article according to claim 6 wherein the amorphous surface layer is chemically non-identical to said non-amorphous base structure.

9. The article according to claim 2, wherein said second film is formed from a material selected from the group consisting of superconducting rare earth-barium-copper oxides, bismuth-strontium-calcium-copper oxides, thallium-bismuth-strontium-calcium-copper-oxides and their precursors.
10. The article of claim 1 wherein the rock-salt-like material is a rock-salt material.
11. The article of claim 10 wherein the rock-salt material is an oxide.
12. The article of claim 11 wherein the oxide is MgO.
13. The article of claim 1 in which the rock-salt-like material is a nitride.
14. The article according to claim 1, wherein said buffer layer comprises a plurality of in-plane and out-of-plane aligned films, and wherein said first film provides a template for the epitaxial growth of each of the others of said plurality of films.
15. The article according to claim 1, wherein said buffer layer comprises a third in-plane and out-of-plane aligned film, and wherein said first film provides a template for the epitaxial growth of said second and third films.
16. The article according to claim 1, wherein the thickness of the first film is less than about 200 angstroms and greater than about 20 angstroms and its alignment is better than about 13 degrees.
17. A method of forming a composite article comprising the steps of:
forming a buffer layer comprising a first thin film
formed on a smooth amorphous surface of a substrate,
from a material having a rock-salt-like structure and substantial alignment both in-plane and out-of-plane,

by ion-beam assisted deposition of said rock-salt-like material under first conditions of temperature, rock-salt-like material evaporation rate, ion energy and flux selected to promote formation of in-plane aligned crystallites of said rock-salt-like material on said smooth amorphous surface at the nucleation stage of film formation and subsequent pseudo-columnar growth of columns of said crystallites; and

forming a second film having substantial alignment both in-plane and out-of-plane on a surface of said buffer layer, wherein said first film provides a template for the epitaxial growth of said second film.

18. The method of claim 17 wherein the rock-salt-like material is a rock-salt material.

19. The method of claim 17 wherein said second film is formed from a material selected from the group consisting of superconductors, semiconductors, photovoltaic materials, magnetic materials, and precursors of superconductors

20. The method of claim 17 further comprising the step of ending the ion beam assistance after the thickness of said first film is such that said smooth amorphous surface is substantially covered with said in-plane aligned crystallites and before the thickness of said first film is about twice the thickness at which said surface is substantially covered with said in-plane aligned crystallites.

21. The method of claim 20 further comprising the step of thereafter forming a homo-epitaxial layer of said rock-salt-like material on the surface of said first film by deposition of said rock-salt material under second conditions of temperature and rock-salt material evaporation rate which are elevated in relation to said first conditions, said first film providing a template for the growth of said homoepitaxial layer.

22. The method of claim 20 further comprising the step of thereafter forming additional in-plane and out-of-plane aligned buffer layer films of additional

materials on the surface of said first film, said first film providing a template for the epitaxial growth of said additional films.

23. The method of claim 17 wherein the RMS of said smooth surface of said substrate is less than about 100 Å.

24. The method of claim 17 wherein said first conditions of temperature are a substrate temperature in the range of about 0°C to about 400°C.

25. A thin film for subsequent epitaxial thin film deposition comprising an smooth amorphous surface; and
a thin film of a material having a rock-salt-like structure formed on said smooth amorphous surface with both in-plane and out-of-plane alignment.

26. A thin film as in claim 25 in which the material having a rock-salt-like structure has a rock salt structure.

27. A thin oxide film as in claim 25 in which the amorphous surface is Si_3N_4 .

28. A structure as in claim 25 in which the base structure is a wire, ribbon or sheet.

29. A structure as in claim 25 in which the material having a rock salt like structure is MgO .

30. A structure as in claim 25 in which the amorphous surface is Hastelloy.

31. A structure as in claim 25 in which the amorphous surface structure is Metglas.

AMENDED CLAIMS

{received by the International Bureau on 20 May 1999 (20.05.99);
original claim 17 amended; remaining claims unchanged (4 pages)}

1. An article, comprising:
 - a substrate having at least one smooth amorphous surface;
 - a buffer layer comprising a first thin film formed on said amorphous surface of said substrate from a material having a rock-salt-like structure and substantial alignment both in-plane and out-of-plane; and
 - a second film having substantial alignment both in-plane and out-of-plane formed on a surface of said buffer layer, wherein said first film provides a template for the epitaxial growth of said second film.
2. An article according to claim 1 wherein said second film is formed from a material selected from the group consisting of superconductors, semiconductors, photovoltaic materials, magnetic materials, and precursors of superconductors.
3. An article according to claim 1 wherein the RMS of said smooth surface is less than about 100 angstroms.
4. An article according to claim 1 wherein the substrate comprises a polycrystalline non-amorphous base structure having an amorphous surface layer.
5. The article according to claim 4, wherein the base structure is formed from a material selected from the group consisting of alloys comprising nickel.
6. The article according to claim 5, wherein the base structure is formed from a material selected from the group consisting of alloys comprising nickel as a primary component.
7. The article according to claim 6, wherein the base structure is formed from Hastelloy.
8. The article according to claim 6 wherein the amorphous surface layer is chemically non-identical to said non-amorphous base structure.

9. The article according to claim 2, wherein said second film is formed from a material selected from the group consisting of superconducting rare earth-barium-copper oxides, bismuth-strontium-calcium-copper oxides, thallium-bismuth-strontium-calcium-copper-oxides and their precursors.
10. The article of claim 1 wherein the rock-salt-like material is a rock-salt material.
11. The article of claim 10 wherein the rock-salt material is an oxide.
12. The article of claim 11 wherein the oxide is MgO.
13. The article of claim 1 in which the rock-salt-like material is a nitride.
14. The article according to claim 1, wherein said buffer layer comprises a plurality of in-plane and out-of-plane aligned films, and wherein said first film provides a template for the epitaxial growth of each of the others of said plurality of films.
15. The article according to claim 1, wherein said buffer layer comprises a third in-plane and out-of-plane aligned film, and wherein said first film provides a template for the epitaxial growth of said second and third films.
16. The article according to claim 1, wherein the thickness of the first film is less than about 200 angstroms and greater than about 20 angstroms and its alignment is better than about 13 degrees.
17. A method of forming a composite article comprising the steps of:
forming a buffer layer, comprising a first thin film on a smooth amorphous surface of a substrate, from a material having a rock-salt-like structure,
by ion-beam assisted deposition of said rock-salt-like material under first conditions of temperature, rock-salt-like material evaporation rate, ion energy and flux selected to promote formation of in-plane aligned crystallites of said rock-salt-like

material on said smooth amorphous surface at the nucleation stage of film formation and subsequent pseudo-columnar growth of columns of said crystallites to provide substantial alignment of the rock-salt-like structure; and

forming a second film having substantial alignment both in-plane and out-of-plane on a surface of said buffer layer, wherein said first film provides a template for the epitaxial growth of said second film.

18. The method of claim 17 wherein the rock-salt-like material is a rock-salt material.

19. The method of claim 17 wherein said second film is formed from a material selected from the group consisting of superconductors, semiconductors, photovoltaic materials, magnetic materials, and precursors of superconductors

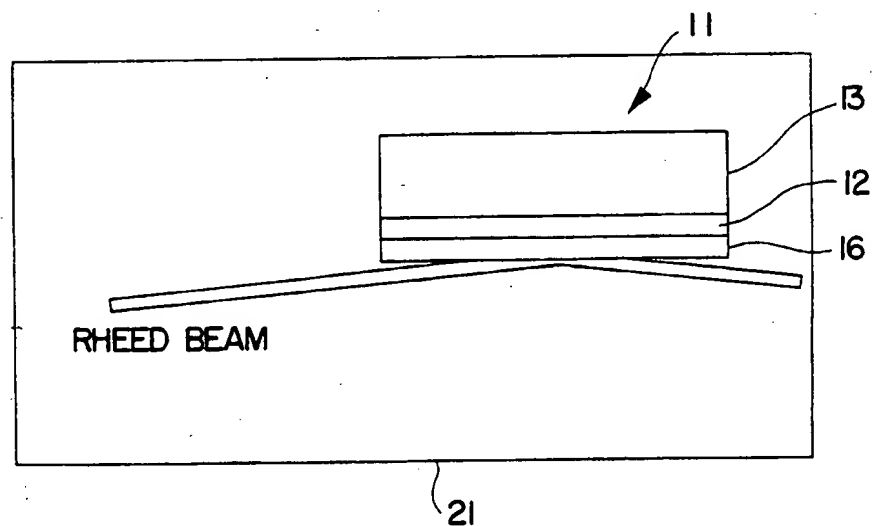
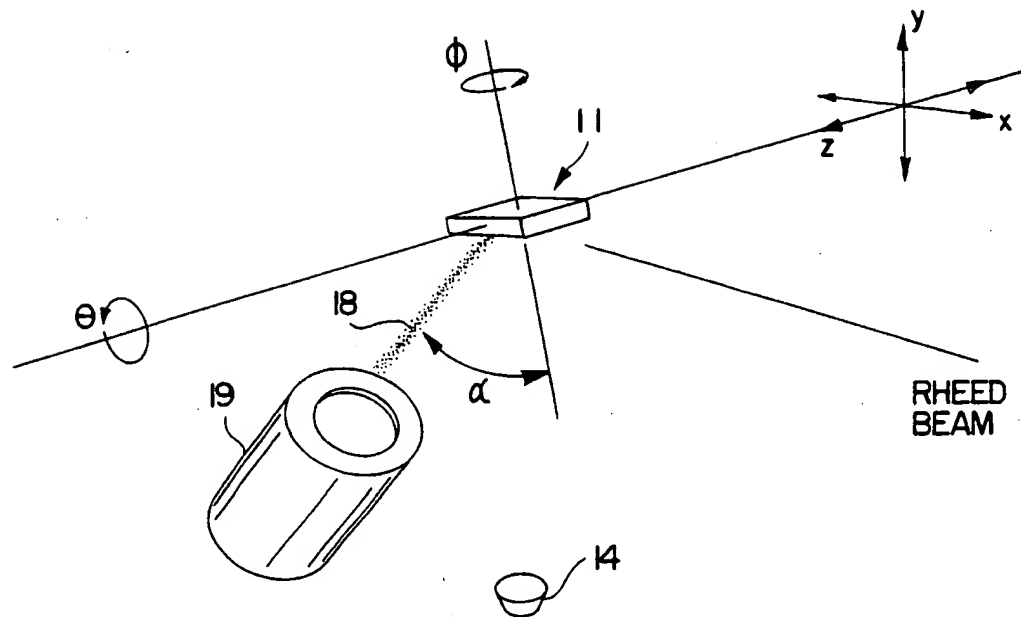
20. The method of claim 17 further comprising the step of ending the ion beam assistance after the thickness of said first film is such that said smooth amorphous surface is substantially covered with said in-plane aligned crystallites and before the thickness of said first film is about twice the thickness at which said surface is substantially covered with said in-plane aligned crystallites.

21. The method of claim 20 further comprising the step of thereafter forming a homo-epitaxial layer of said rock-salt-like material on the surface of said first film by deposition of said rock-salt material under second conditions of temperature and rock-salt material evaporation rate which are elevated in relation to said first conditions, said first film providing a template for the growth of said homoepitaxial layer.

22. The method of claim 20 further comprising the step of thereafter forming additional in-plane and out-of-plane aligned buffer layer films of additional materials on the surface of said first film, said first film providing a template for the epitaxial growth of said additional films.

23. The method of claim 17 wherein the RMS of said smooth surface of said substrate is less than about 100 Å.
24. The method of claim 17 wherein said first conditions of temperature are a substrate temperature in the range of about 0°C to about 400°C.
25. A thin film for subsequent epitaxial thin film deposition comprising
an smooth amorphous surface; and
a thin film of a material having a rock-salt-like structure formed on said smooth amorphous surface with both in-plane and out-of-plane alignment.
26. A thin film as in claim 25 in which the material having a rock-salt-like structure has a rock salt structure.
27. A thin oxide film as in claim 25 in which the amorphous surface is Si_3N_4 .
28. A structure as in claim 25 in which the base structure is a wire, ribbon or sheet.
29. A structure as in claim 25 in which the material having a rock salt like structure is MgO .
30. A structure as in claim 25 in which the amorphous surface is Hastelloy.
31. A structure as in claim 25 in which the amorphous surface structure is Metglas.

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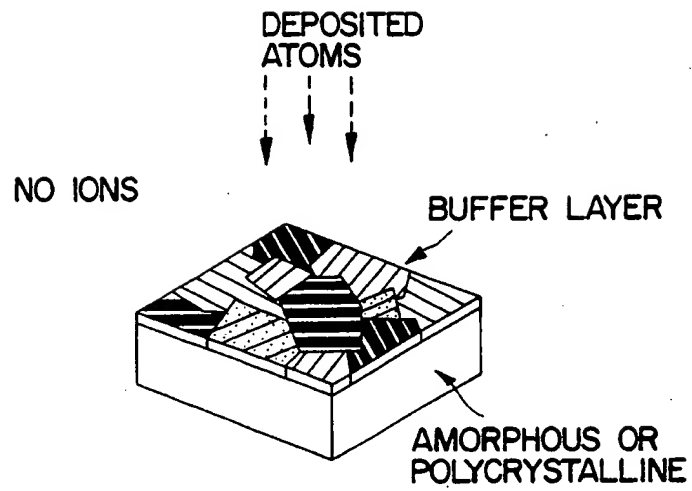


FIG. 3

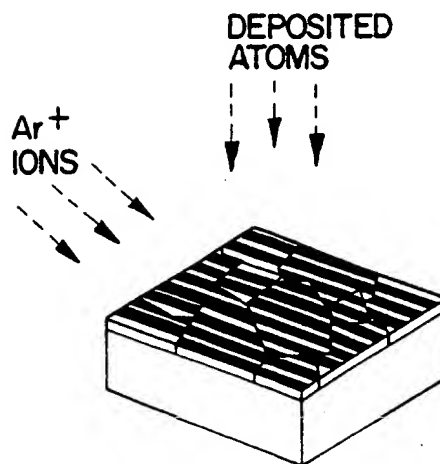


FIG. 4

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FIG. 5a

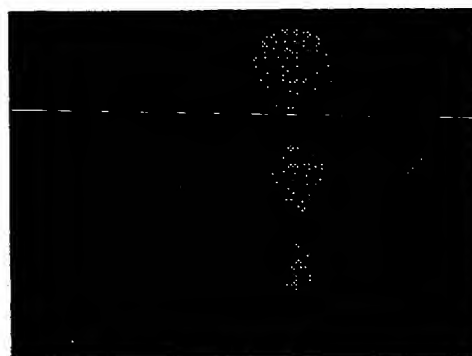


FIG. 5d

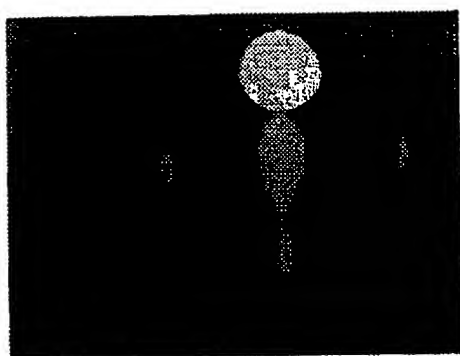


FIG. 5b

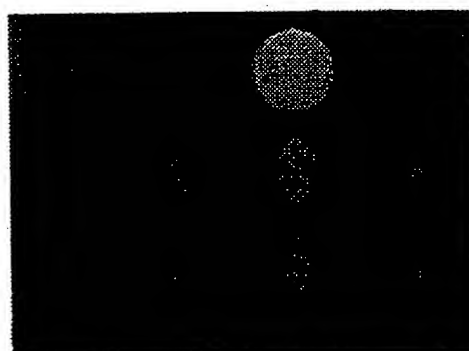


FIG. 5e



FIG. 5c



FIG. 5f

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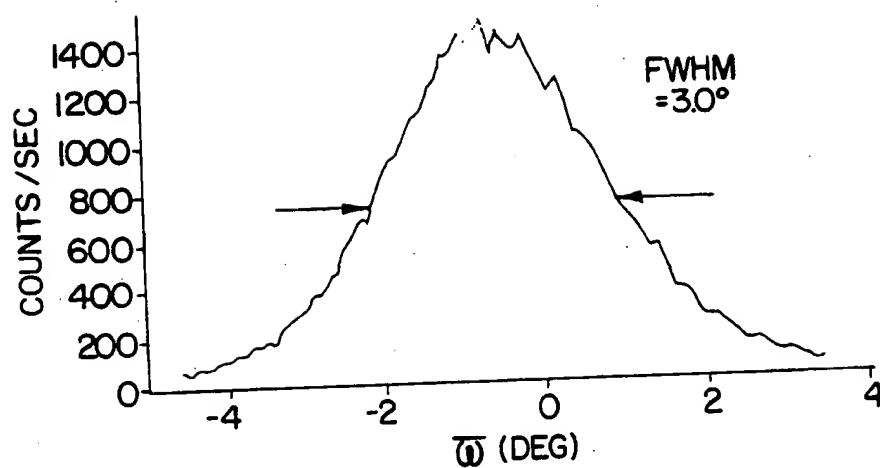


FIG. 6A

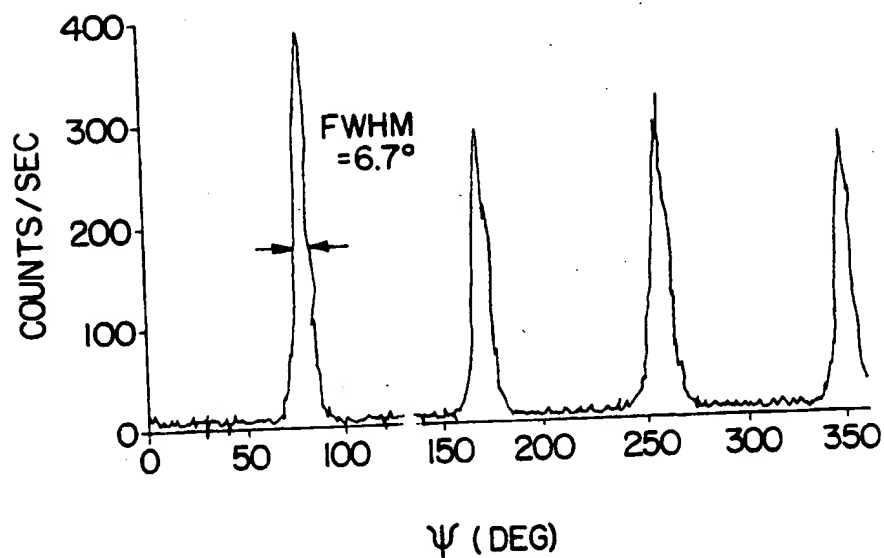


FIG. 6B

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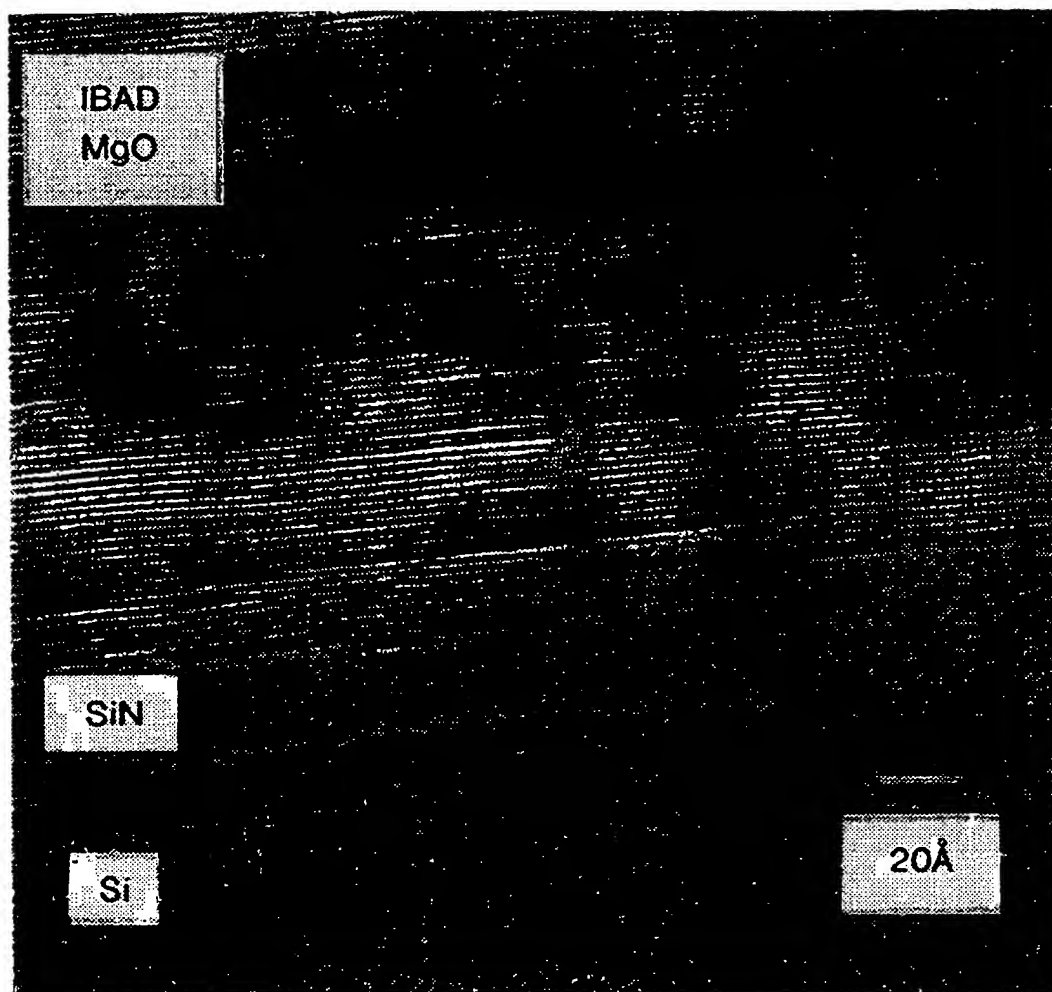


FIG. 7

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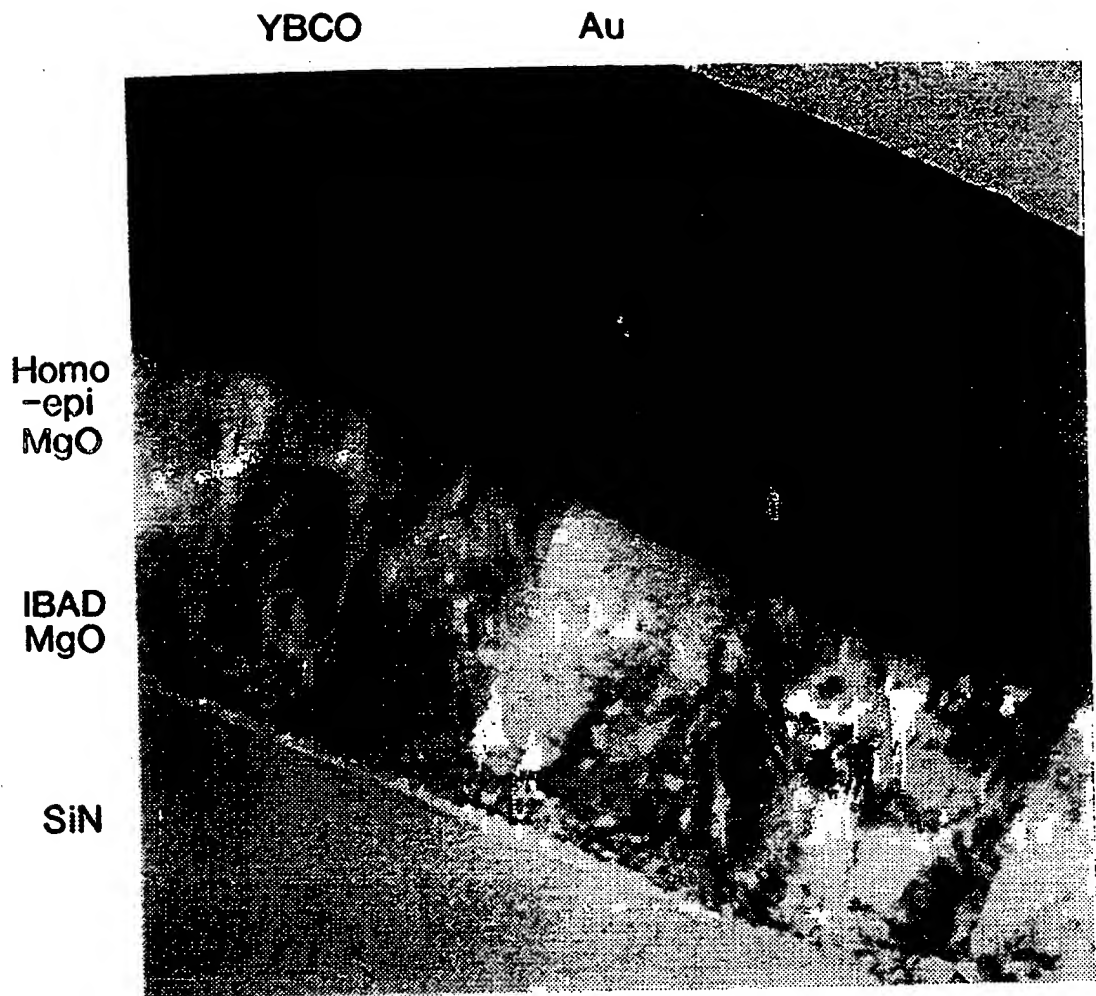


FIG. 8

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/24194

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C30B23/02 C30B29/16 C30B29/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C30B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 669 411 A (SUMITOMO ELECTRIC INDUSTRIES LTD) 30 August 1995	1,2,5-7, 9-12,14, 25,26, 28-30
Y	see claims 1,4,5; example 5	17
X	PATENT ABSTRACTS OF JAPAN vol. 13, no. 338 (E-795), 28 July 1989 & JP 01 099268 A (MITSUBISHI ELECTRIC CORP), 18 April 1989 see abstract	1,2, 9-12,25, 26,29

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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Date of the actual completion of the international search

18 March 1999

Date of mailing of the international search report

25/03/1999

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Authorized officer

Cook, S

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/24194

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	HE ET AL.: "Deposition of biaxially oriented metal and oxide buffer layer films on textured Ni tapes: new substrates for high current high temperature superconductors" PHYSICA C., vol. 275, 10 February 1997, pages 155-161, XP004114521 AMSTERDAM NL see page 156, right-hand column ----	17
A	EP 0 410 627 A (KABUSHIKI KAISHA TOSHIBA) 30 January 1991 see claim 1 ----	17
A	MAO ET AL.: "Ion beam assisted deposition of biaxially textured YSZ thin films as buffer layers for YBCO superconducting films" PHYSICA C., vol. 282-287, August 1997, pages 611-612, XP004130427 AMSTERDAM NL see the whole document ----	17
A	YANG ET AL.: "Control of in-plane alignment and the critical current of polycrystalline YBa ₂ Cu ₃ O _{7-x} " APPLIED SUPERCONDUCTIVITY., vol. 3, no. 1-3, January 1995, pages 105-111, XP004062136 EXETER GB see the whole document -----	17

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/US 98/24194

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 669411	A	30-08-1995	JP 7291626 A	07-11-1995
			CA 2143265 A,C	26-08-1995
			US 5607899 A	04-03-1997
<hr/>				
EP 410627	A	30-01-1991	JP 3188604 A	16-08-1991
			US 5607781 A	04-03-1997
<hr/>				

Form PCT/ISA210 (patent family annex) (July 1992)

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